

AMENDMENTS TO THE SPECIFICATION

[0007] U.S. Patent No. 3,779,851 discloses a composite laminate constituted of a plurality of graphite fiber sheets impregnated with epoxide resin. This laminate is presented as having a very high mechanical strength to weight ~~mechanical strength to weight~~ ratio, as well as very low thermal expansion properties. Such specifications are desired for applications of these composite laminates in the manufacture of optical instruments (mirror). These are also extremely rigid composite laminates. The total thickness of the composite laminates according to U.S. 3,779,851 is 3.6 mm, for example, even 3 mm as a minimum (12 inches x 0.254). The sheets ~~folds~~ used to manufacture this laminate are sheets preimpregnated with carbon fibers in an epoxy resin matrix. This composite laminate has a too substantial stiffness to be used as raw material in the manufacture of sports articles, such as boots, for example, where a certain deformability or bending ability in the longitudinal direction is needed. In addition, the fibrous reinforcement is exclusively made of carbon fibers. This results in a prohibitive cost for fields of application such as that of sports articles, which are produced at large scale and at very low cost, contrary to what can be found in frontier technological fields, such as aeronautics or aerospace.

[0009] Thus, the French Patent Application Publication No. 2 742 063 discloses a roller skate chassis having a shock absorbing means, constituted by a laminate including, successively, a rigid stress layer and a viscoelastic layer. The laminate can include one or several pairs of rigid

layer/viscoelastic layer. ~~rigid layer/viscoelastic layer.~~ The rigid layer is made of a plastic material having a high modulus of elasticity, from composite fibers or from aluminum, these materials being selected for their rigidity or their lightweight. The viscoelastic layer is made of rubber or of synthetic elastomer. To obtain the desired shock absorbing effect, the composite-rubber laminate according to FR 2 742 063 necessarily has a thickness greater than or equal to 3 mm. Moreover, this composite laminated shock absorbing means remains perfectible in terms of deformability, cost, and weight gain.

[0010] The French Patent Application Publication No. 2 730 416 describes a golf club shaft constituted by a laminate having a composite outer layer made of resin reinforced with:

- carbon fibers, a central core (or central member) made of polymer foam, synthetic or natural resin, cork, wood or the like; and
- an inner composite layer made of glass fiber-reinforced resin.

The density of the composite inner and outer layers is greater than 1.2 kg/dm³ and their longitudinal Young's modulus E1 is greater than 20 Gpa. The polymer foam core has a density lower than 1.2 kg/dm³ and a longitudinal Young's modulus E3 lower than 20 Gpa. This composite laminate has a thickness between 0.2 and 9 mm. Here again, it has been found that the stiffness/deformability/durability/weight gain ~~stiffness/deformability/durability/weight gain~~ compromise is not entirely satisfactory for this composite/polymer foam/composite laminate according to this French Patent Application Publication No. 2 730 416.

[0026] According to a preferred arrangement of the invention, the core 2 and layers 3 and 4 are each constituted by a plurality of plies ~~folds~~ - in this case 3 for the core 2 (2₁, 2₂, 2₃) and 4 for the layers 3 and 4 (3₁, 3₂, 3₃, 3₄; 4₁, 4₂, 4₃, 4₄, respectively). In practice, the core 2 and/or the layer(s) 3 and 4 are obtained by superimposing a plurality of plies ~~folds~~ of fibrous and/or composite materials. Thus, the composite laminate 1 according to the invention has one or several plies ~~folds~~ forming the core, or one or several plies ~~folds~~ forming the layers, these plies ~~folds~~ being formed by sheets ~~plies~~ of micro-fibers that are woven or non-woven, ~~unwoven~~, oriented or non-oriented, preimpregnated or non-preimpregnated with resin.

[0030] With respect to the type and structure of the fibrous material of the core 2, it must be noted that the reinforcement fibers of this core 2 are woven or non-woven, ~~unwoven~~, oriented in one or more directions or non-oriented, and are preferably selected from the group including:

- the textile (micro)fibers made of:
 - synthetic polymers: polyamides (NYLON®), polyolefine, polyesters, polyesterimides...
 - natural polymers: silk, cotton, linen, jute, hemp,
- the cellulose fibers.

[0031] By way of examples of fibrous reinforcement for the core 2, one can cite all of the natural or synthetic fabrics, in particular silk, polyamides (NYLON®), such as a textile used as a lining in garments, for example, and constituted of an non-woven ~~unwoven~~ material made of nylon micro-fibers (CAMBRELLE®), or other textiles such as linen, cotton, jute, leno,

BEMBERG®; any type of paper: aquarelle paper, blotting paper, kraft paper, absorbent paper, toilet paper, newsprint, e.g.; any type of carton.

[0032] In fact, suitable are all of the fibrous materials which can be in the form of fine sheets ~~plies~~ and can be impregnated ~~can be impregnated~~ with polymer resin, and capable of forming the fibrous reinforcement of the core 2 of the laminate according to the invention, provided that it has low market value.

[0033] With respect to the fibrous reinforcement of the layers, the fibers of which it is made, whether they are woven or non-woven, ~~unwoven~~, oriented in one or several directions or non-oriented, are preferably selected, according to the invention, from the group of high performance (micro)fibers including:

- carbon (micro)fibers;
- glass (micro)fibers;
- synthetic polymer (micro)fibers, in particular polyolefines, more specifically oriented and stretched high density polyethylene fibers DYNEEMA®, polyamide fibers KEVLAR® TEVARON®, and other fibers such as VECTRAN® or SPECTRA®;
- metallic (micro)fibers, in particular aluminum, titanium or boron (micro)fibers;
- natural (micro)fibers such as silk.

Possibly, one can envision using mixtures of these fibers.

[0036] In the sense of the invention, this notion of lesser quality or mechanical strength can be perceived through at least one of the following mechanical properties specific to the fibers forming the fibrous reinforcement of the core 2; ~~and of the layers:~~

- the micro-fibers of the core 2, woven or non-woven, ~~unwoven~~, oriented in one or several directions or non-oriented, have a characteristic of rupture stress CR (in Mpa) in longitudinal traction such that:

$$CR \leq 1\,500$$

preferably

$$CR \leq 1\,000$$

and even more preferably

$$CR \leq 750$$

- the micro-fibers of the core 2, ~~layer(s)~~, woven or unwoven, oriented in several directions or non-oriented, have a modulus M (in Mpa) in longitudinal traction such that:

$$M \leq 50\,000$$

preferably

$$M \leq 30\,000$$

and even more preferably

$$M \leq 20\,000$$

- the micro-fibers of the core 2, ~~layer(s)~~, woven or unwoven, oriented in several directions or non-oriented, have an elongation at rupture AR (in %) in longitudinal traction, such that:

$$AR \geq 1.0$$

preferably

$$AR \geq 1.5$$

and even more preferably

$$AR \geq 2.0.$$

[0041] Thus, these matrices/binders are selected, for example, from among the organic thermohardening or thermoplastic resins:

<u>· phenolic;</u>	○ phenolic;
<u>· polyester;</u>	○ polyester;
<u>· vinylester;</u>	○ vinylester;
<u>· polyesterimide;</u>	○ polyesterimide;
<u>· polyaramide;</u>	○ polyaramide;
<u>· epoxide;</u>	○ epoxide;
<u>· polyamide;</u>	○ polyamide;
<u>· polycarbonate;</u>	○ polycarbonate;
<u>· polyterephthalate;</u>	○ polyterephthalate;
<u>· polyphenylene oxide;</u>	○ polyphenylene oxide;
<u>· polyacetal;</u>	○ polyacetal;
<u>· polyamide;</u>	○ polyamide;
<u>· polysulphide;</u>	○ polysulphide;
<u>· polyolefine.</u>	○ polyolefine.

[0051] In the first embodiment, dried fibrous reinforcements (mats, plies of strands oriented in one or several directions, fabrics) are used. The fibrous reinforcement of the core 2 is thus constituted by one or several superimposed sheets (of paper, for example) or of fabrics (silk, for example) or of non-woven, for example, CAMBRELLE® = nylon micro-fibers. Each layer 3 and 4 has a fibrous reinforcement that is constituted of one or several plies ~~folies~~ of a fibrous material (carbon fibers, oriented or non-oriented, woven or non-woven). ~~unwoven~~). All or part

of the plies ~~folde~~s of the layers 3-4 and possibly of the core 2 are impregnated with a cross-linkable resin (for example, epoxide resin). The stack of resin impregnated plies ~~folde~~s is subject to high pressure (for example, 8 bars). Advantageously, heat is applied to accelerate cross-linking (for example at 150°C). Preferably, the dried core is arranged between the layers, and both layers are then impregnated with resin.

[0052] According to the second embodiment of the method, the ply(ies) ~~fold(s)~~ forming the layer(s) 3-4 and/or the core 2, are constituted by a resin-preimpregnated fibrous material.

The stacking is then undertaken to obtain the micro-sandwich; pressure and possibly heat are applied as provided in the first embodiment. For the layers, the preimpregnated fabric used can be a multidirectional or unidirectional fabric of carbon fibers on which the resin is deposited. The excess of resin is eliminated via passage between rollers which are heated or non-heated (calendering). Before use, the product must be kept refrigerated, generally below 18°C to avoid resin polymerization. The fabrics must be brought back to the ambient temperature in order to be used. When the fibrous reinforcement of the layers 3-4 is not made of carbon fibers but of high-density polyethylene fibers, the pressure used is 2 bars and the temperature is 100°C. In any event, the person with ordinary skill in the art is capable of adjusting these parameters depending on the types of materials used.

[0058] By means of a hole punching tool having the shape of the element 12 of FIG. 3A, six sheets ~~folde~~s of preimpregnated carbon fabric and four sheets ~~folde~~s of Cumbrouly are cut. Three sheets ~~folde~~s of preimpregnated carbon fabric are stacked to form the outer layer 4, then four sheets ~~folde~~s of Cumbrouly are stacked to form the core 2, and finally three sheets ~~folde~~s of preimpregnated carbon fabric are stacked to form the other outer layer 3.

[0059] This stack or superimposition of sheets/plies ~~fold~~s is then placed in the female portion of an appropriately shaped mold; the male portion of this mold is then applied on the stack or superimposition of sheets/plies ~~fold~~s by means of a flat press of the type of those commercialized by SATIM corporation, applying heat at 150°C for 10 minutes and pressure at 4 bars.